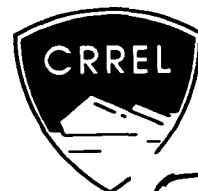


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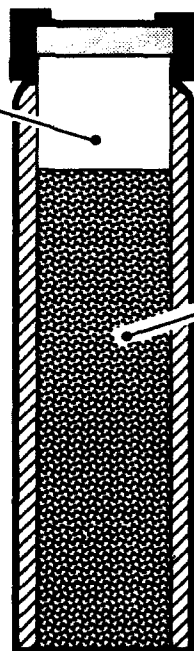
# Aqueous Extraction- Headspace/Gas Chromatographic Method for Determination of Volatile Organic Compounds in Soils

Alan D. Hewitt, Paul H. Miyares, Daniel C. Leggett  
and Thomas F. Jenkins

April 1992

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Headspace



Aqueous Dispersed  
Soil Mixture

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Distribution Unlimited

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*For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.*

*Cover: Volatile organic compound sample vial.*



**U.S. Army Corps  
of Engineers**  
Cold Regions Research &  
Engineering Laboratory

## **Aqueous Extraction-- Headspace/Gas Chromatographic Method for Determination of Volatile Organic Compounds in Soils**

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## **PREFACE**

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Branch, Paul H. Miyares, Daniel C. Leggett and Dr. Thomas F. Jenkins, Research Chemists, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory.

Funding for this work was provided by the U.S. Army Toxic and Hazardous Materials Agency, Durant Graves, Project Monitor. The authors wish to thank Dr. T.M. Spittler for providing the information concerning headspace/gas chromatography, Dr. S.G. Pavlostathis for providing a contaminated soil and insightful comments, and Dr. C.L. Grant and Marianne Walsh for critical review of the text.

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# Aqueous Extraction-Headspace/Gas Chromatographic Method for Determination of Volatile Organic Compounds in Soils

ALAN D. HEWITT, PAUL H. MIYARES, DANIEL C. LEGGETT AND THOMAS F. JENKINS

## INTRODUCTION

Volatile Organic Compounds (VOCs) are the most frequently encountered contaminants at hazardous waste sites (Plumb and Pitchford 1985, Zarrabi et al. 1991), and because of their pervasiveness and transience in soils, VOCs have drawn considerable attention. Currently, protocols specify the collection of bulk soil samples from which subsamples are removed in the laboratory for VOC analysis (U.S. EPA 1986), albeit the process of obtaining subsamples has shown, in some cases, to allow volatilization losses in excess of 80% of the VOCs present (Urban et al. 1989, Siegrist and Jennsen 1990). Recently, Lewis et al. (1991) have recommended that samples collected for VOC analysis be placed directly into specially designed analysis vessels or appropriate bottles containing methanol (MeOH). Another current practice is the shipment of soils from hazardous waste sites for VOC characterization in contract laboratories without screening collected samples. Consequently, many samples render "below detection" or background concentrations. Screening of soils in the field would permit more efficient selection of samples for certified laboratory analysis, and field analysis methods capable of providing determinations comparable to existing laboratory techniques would allow for timely decisions to be made on site (Spittler et al. 1985, Marrin 1985).

A Headspace/Gas Chromatographic (HS/GC) method, well-suited for on-site screening of VOCs, has been the subject of several recent papers (Kiang and Grob 1986, Robbins et al. 1987, Griffith et al. 1988, Stuart et al. 1991). Results comparable to Purge-and-Trap/Gas Chromatographic (PT/GC)

VOC analysis of aqueous samples have been reported (Stuart et al. 1991, Dietz and Singley 1979). Method comparisons for soil samples, however, suffer from the heterogeneity of field samples, or have only been done with soils treated directly with MeOH doped spikes (Hewitt et al. 1991). Additionally, critical variables such as holding time and extent of sample disturbance were often not held constant.

This study compares the measured levels of four VOCs in two laboratory-fortified soils, and TCE in two field soils. Laboratory-treated soils were spiked by a vapor fortification procedure that is analogous to the exposure of unsaturated soils to spills in which a separate contaminant phase exists (Hewitt et al. 1991, Jenkins and Schumacher 1987). We chose trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), benzene (Ben) and toluene (Tol) to represent contaminant on with petroleum products and industrial solvents. Some relevant physical properties are given in Table 1.

The sample preparation and analysis methods compared in this study were aqueous extraction-HS/GC-Photoionization Detection (PID) and Method 8240, PT/GC-Mass Spectrometer (MS) detection (U.S. EPA 1986). Aqueous-HS/GC sample preparation and analysis was streamlined for field applications using water as the extracting agent, hand shaking agitation to partition the VOCs and a portable GC. Method 8240 specifies two sample handling procedures to prepare soils for analysis, depending on the anticipated VOC concentrations (U.S. EPA 1986). For anticipated concentrations of greater than 1 µg/g, samples are extracted with methanol (MeOH) and an aliquot of the extract is analyzed. For samples expected to

contain less than 1  $\mu\text{g/g}$ , the sample is added directly to a special vessel from which VOCs are purged after adding water and heating the slurry to 40°C. Overall, this method comparison involves the following operational variables: MeOH versus water as extracting solvents, dynamic versus static phase partitioning, heating versus room temperature, and different methods of separation and detection. Since the latter two parameters (separation and detection) are inter-method consistent (i.e., samples and standards see the same treatment), the comparison will primarily reveal any difference between MeOH and water as extractors of VOCs from soil with greater than 1- $\mu\text{g/g}$  analyte levels, and between a static room temperature and heated (40°C) dynamic water extraction for concentrations less than 1  $\mu\text{g/g}$ .

## MATERIALS AND METHODS

### Vapor fortification treatment

Two soils (the U.S. Army Toxic and Hazardous Materials Agency [USATHAMA] standard soil no. AO46 and a soil obtained from Point Barrow, Alaska) were fortified using a vapor treatment method (Hewitt et al. 1991, Jenkins and Schumacher 1987). Characteristics of these soils are listed in Table 2. No VOCs were detectable in either soil prior to fortification. To attain appropriate concentrations, high-level samples used 2.00 g of soil, whereas 1.00 g was used for the low-level samples. Soils were weighed into 40-mL VOA vials and positioned uncapped on a perforated aluminum plate inside a large desiccator. An open petri dish containing the fortification solution was placed under the samples (Fig. 1). Empty vials were included to check for sorption onto vial walls. Vapor fortification treatment periods were 4 and between 39–46 days.

The stock fortification solution was prepared by combining reagent grade Tol (1.21 g), TDCE (0.503 g), TCE (0.586 g) and Ben (0.351 g) in MeOH and diluting to 100 mL in a volumetric flask. Concentrations of VOCs in the soils ranging from 100–1000  $\mu\text{g/g}$  were obtained after exposure to the equilibrium vapor above a 50-mL aliquot of the stock solution in the fortification chamber. A second

Table 1. Physical properties of the compounds of interest.

Characteristic	Compound			
	TDCE	TCE	Ben	Tol
Boiling point (°C)	48a	86.7a	80.1a	111a
$K_{ow}$ (mL/mL)*	123c	195(20)b†	135(20)a	490(20)a
Solubility in water (mg/L)	600(20)a	1100(25)a	1780(20)a	515(20)a
Henry's Law (atm m <sup>3</sup> /mol)	0.0090(20)d	0.010(20)d	0.0074(20)d	0.0059(20)d

\*  $K_{ow}$ —octanol/water partition coefficient.

† Table values in parentheses are the corresponding temperatures (°C).

a. Verschueren (1983)

b. Schwachenbach et al. (1983)

c. Mabey et al. (1982)

d. Yurteri et al. (1987)

high-level fortified soil in the 1- to 100- $\mu\text{g/g}$  concentration range was obtained by exposing the soils to the vapor from a 50-mL aliquot of a 1:1 dilution of the stock solution with tetraethylene glycol dimethyl ether (tetraglyme). Low-level concentrations (0.1–10  $\mu\text{g/g}$ ) were achieved by exposing the soils to vapors from 10-mL aliquots of 1:10 and 1:20 dilutions of the stock solution with tetraglyme.

Each fortification level started with 12 subsamples of each soil and 4 empty vials so that there could be two complete method comparisons on identically treated samples. A comparison set consisted of six subsamples of each soil and two empty vials. This provided triplicate soil samples and a single empty vial for analysis by each method. After removal from the desiccator, the vials were

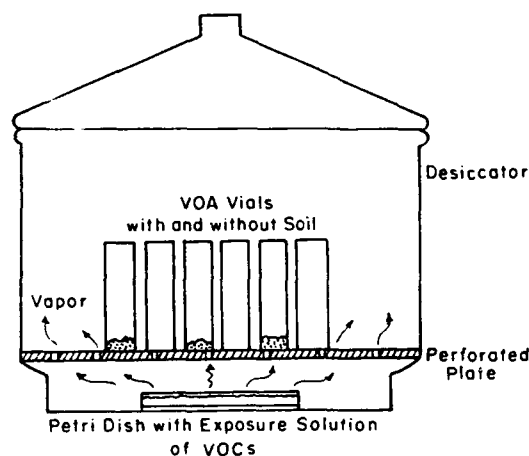


Figure 1. Vapor fortification chamber.

**Table 2. Characteristics of soils.**

Characteristic	USATHAMA standard soil	Point Barrow, Alaska, soil	CRREL soil	Clarkson soil
% Organic carbon	1.45	6.69	0.08	0.13
% Clay	53.6	20.1	<5	12
% Moisture	1.43	2.00	17	22
Dispersion rate (min)*	<0.1	<0.1	<0.1	10

\* Time required to disperse 2 g of soil in 30 mL of water by hand shaking.

aspirated for 10 minutes by placing them along the front edge of an exhaust hood. The velocity of air passing over the uncapped vials was approximately 1.3 m/s (a typical air velocity of a laboratory hood with a 80- × 25-cm opening). This step was necessary because the amount of VOCs remaining in the headspace of each vial was significant. Ten minutes of aspiration lowered the VOCs in empty vials below detection.

### Field samples

Several soil subsamples were collected either 3 ft (1 m) below the surface with a Veihmeyer tube or with a shovel from the surface at CRREL. Samples were taken from locations near known sources of contamination. A second field soil was obtained as a bulk sample (~30 g), from Dr. S.G. Pavlostathis of Clarkson University. This soil was selected because it is so poorly dispersed by water (Table 2) and in a previous study it had demonstrated slow aqueous desorption of TCE (Pavlostathis and Jagal 1991). The Clarkson soil was refrigerated after receipt, and subsampled after 2, 11 and 162 days of storage.

Field soils were rapidly subsampled once brought into contact with the atmosphere by taking 1.5-cm<sup>3</sup> soil plugs with a tipless 10-cm<sup>3</sup> plastic syringe.\* Depending on the method, the soil plugs were placed randomly into VOA vials that contained water, MeOH or were empty. All vials were weighed ahead of time so that the exact weight of the soil subsample could be determined. Six sets of quintuplicate subsamples were collected from the CRREL site, and three sets of triplicate subsamples were removed from the bulk Clarkson soil.

### Standards

The combined analyte solution, previously called the "stock fortification solution," also served as the analytical stock standard for analyses in the 100- to 1000-μg/g concentration range. The stock standard was diluted appropriately for the other concentration ranges (Table 3). The stock solution was

\* Personal communication with Dr. T.M. Spittler, U.S. Environmental Protection Agency, Environmental Services Division—Region 1, Lexington, Massachusetts (1989).

**Table 3. Volumes of stock standard used for the different ranges of expected VOC concentrations in the soil.**

Working standard	Vol. of working std. used for calibration (μL)	Vol. of MeOH extract or headspace used for analysis (μL)	Conc. range for VOCs in soil (μg/g)
<b>HS/GC/PID*</b>			
1/100 Stock†	2.5–160	100	0.1–10
1/10 Stock	10–80	25	1–100
Stock	50–200	2	100–1000
<b>PT/GC/MS**</b>			
1/10 Stock	10	100	1–100
Stock	10	10	100–1000

\*HS/GC/PID—headspace/gas chromatograph/photoionization detector.

†Stock: 1.21 g Toluene, 0.503 g trans-1,2-dichloroethylene, 0.586 g trichloroethylene, 0.351 g benzene in 100 mL of MeOH.

\*\*PT/GC/MS—purge-and-trap/gas chromatograph/mass spectrometer.



refrigerated at 4°C, and dilutions prepared daily as needed. A new stock was prepared monthly. Both instrumental methods used the same analytical standards for calibration.

### Extraction and analysis of VOCs present in soils

#### *Aqueous extraction-HS/GC analysis*

Consistent with previous studies\* (Dietz and Singley 1979), samples and blanks were extracted with 30 mL of deionized water (Type 1, Millipore Corp.). Equilibrium headspace concentrations were developed by vigorously shaking the VOA vials by hand for 2 minutes, or in the case of the Clarkson soil, until the sample appeared dispersed (~10 min.). Volumes of equilibrium headspace, transferred in gas-tight syringes (Hamilton), ranging from 2 to 100  $\mu$ L (Table 3), were analyzed by direct injection. The syringe was flushed several times with headspace air before we removed a volume twice the size needed for analysis. Immediately after withdrawing the syringe, we set the proper volume and manually injected the vapor into the GC.

We did HS/GC on a field portable PhotoVac GC (PhotoVac, Inc., Model 10S10) equipped with a PID. Baseline resolution of the four test analytes (TDCE, Ben, TCE and Tol) was achieved with a packed column of 10% SE-30 on Chromosorb 80/100 mesh, 30-cm length, 0.32-cm od. The carrier gas was zero grade air flowing at 15 mL/min. Approximate retention times for the compounds were 0.86 minutes for TDCE, 1.8 minutes for Ben, 2.6 minutes for TCE and 4.8 minutes for Tol, allowing repeat analyses every 6 minutes. The samples were prepared and analyzed at room temperature (~24°C).

Sample analyte concentrations were determined by direct comparison to aqueous standards. Peak height responses on a strip chart recorder (Linear Instruments) were used for quantification. The calibration standards were chosen so as to bracket the respective analyte responses. Generally, peak height response was a nonlinear function of concentration, requiring polynomial regression analysis. This portable GC and recorder system is capable of operating off internal dc power and gas supplies for approximately 8 hours.

#### *Method 8240*

The sample preparation protocol for the PT/GC/MS procedure followed EPA SW-846 method 8240 (U.S. EPA 1986). When concentrations were expected to be greater than 1  $\mu$ g/g (high level), we dispersed the soil in 20 mL of MeOH and extracted by mixing for 2 minutes on a wrist-action shaker. After the suspended soil settled for a minimum of 30 minutes, MeOH aliquots (Table 3) were transferred into 5.0 mL of bubble-free water in a 5-mL glass syringe (Hamilton) containing 10  $\mu$ L of 0.425- $\mu$ g/ $\mu$ L benzene-d6 as the internal standard. This solution was then injected into the frit of the purge-and-trap system. Samples with expected concentrations less than 1  $\mu$ g/g were capped with a modified purge-and-trap 40-mL VOA vial lid.\* This VOA vial lid serves as a vapor barrier until attached to a purge-and-trap system (Lewis et al. 1991). After attaching the VOA vial, we introduced by syringe 5.0 mL of bubble-free water spiked with 5.0  $\mu$ L of the benzene-d6 internal standard. While purging, the VOA vial is submerged up to the cap in a 40°C water bath. The only deviation from SW-846 guidelines was the use of a vortex mixer for dispersing the Clarkson soil in MeOH instead of by mechanical shaking.

The purge-and-trap system consisted of a Tekmar liquid sample concentrator (LSC-2) coupled with a model ALS automatic laboratory sampler. Samples and standards were purged for 11 minutes with helium, flowing at a rate of 30 mL/min. The stripped analytes were collected on a 25-cm OV-1 Tenax and silica gel column. The collector was desorbed for 4 minutes at 180°C, followed by bake-out at 225°C for 7 minutes. For maximum precision, a single purge-and-trap chamber was used throughout.

Analytes were separated and determined on a Hewlett-Packard 5890 series II GC, interfaced to a Hewlett-Packard series 5970 mass selective detector. Separation was obtained with 5% SP-1000 on Carbowax (60/80 mesh), 180 cm in length, 0.32-cm od, with ultra-pure helium carrier gas flowing at 30 mL/min. Operating conditions were an injection temperature of 200°C, an initial temperature of 45°C, an initial time of 3 minutes, a ramp rate of 8.0°C/min, a final temperature of 220°C and a final time of 15 minutes. The mass spectrometer was set for full scan from 40 to 300 m/e. Analyses were repeated at a rate of one per hour.

\* Personal communication with Dr. T.M. Spittler, U.S. Environmental Protection Agency, Environmental Services Division-Region 1, Lexington, Massachusetts (1989).

\* Associated Design & Manufacturing Company, Alexandria, Virginia.

**Table 4. Inter-method comparison of TDCE, Ben, TCE and Tol ( $\mu\text{g/g}$ ) for high-level fortified soils.**

<b>a. Mean concentrations and standard deviations for vapor treatment, undiluted MeOH stock (<math>\mu\text{g/g}</math>)</b>				
	<i>4 days exposure</i>		<i>39 days exposure</i>	
	<i>HS/GC</i>	<i>PT/GC/MS</i>	<i>HS/GC</i>	<i>PT/GC/MS</i>
<b>USATHAMA standard soil</b>				
TDCE	72.8 $\pm$ 5.9	66.0 $\pm$ 2.6*	135 $\pm$ 11	122 $\pm$ 19*
Ben	117 $\pm$ 6.5	94.3 $\pm$ 2.2	184 $\pm$ 4.0	177 $\pm$ 34*
TCE	214 $\pm$ 9.8	202 $\pm$ 16*	372 $\pm$ 9.5	380 $\pm$ 105*
Tol	492 $\pm$ 21.0	529 $\pm$ 56*	885 $\pm$ 50	1660 $\pm$ 427
<b>Point Barrow, Alaska, soil</b>				
TDCE	148 $\pm$ 4.0	170 $\pm$ 9.7	225 $\pm$ 10	230 $\pm$ 12*
Ben	198 $\pm$ 10	204 $\pm$ 5.0*	256 $\pm$ 14	281 $\pm$ 32*
TCE	319 $\pm$ 27	444 $\pm$ 12	416 $\pm$ 24	613 $\pm$ 57
Tol	689 $\pm$ 76	1120 $\pm$ 5.8	927 $\pm$ 63	2740 $\pm$ 61
<b>b. Mean concentrations and standard deviations for vapor treatment, 50:50 mixture of MeOH stock and tetraglyme (<math>\mu\text{g/g}</math>)</b>				
	<i>4 days exposure</i>		<i>39 days exposure</i>	
	<i>HS/GC</i>	<i>PT/GC/MS</i>	<i>HS/GC</i>	<i>PT/GC/MS</i>
<b>USATHAMA standard soil</b>				
TDCE	1.63 $\pm$ 0.11†	1.84 $\pm$ 0.66*	1.71 $\pm$ 0.15	4.93 $\pm$ 1.34
Ben	8.75 $\pm$ 0.19	5.67 $\pm$ 1.30	8.75 $\pm$ 0.09	7.33 $\pm$ 1.42*
TCE	11.7 $\pm$ 0.40	9.22 $\pm$ 1.68*	11.6 $\pm$ 0.29	15.1 $\pm$ 2.4*
Tol	42.9 $\pm$ 1.50	33.3 $\pm$ 3.8	43.4 $\pm$ 2.2	41.4 $\pm$ 4.9*
<b>Point Barrow, Alaska, soil</b>				
TDCE	12.3 $\pm$ 0.40	12.5 $\pm$ 1.8*	11.7 $\pm$ 0.70	19.1 $\pm$ 0.70
Ben	29.1 $\pm$ 2.9	22.0 $\pm$ 3.0	26.7 $\pm$ 0.29	26.0 $\pm$ 1.9*
TCE	34.1 $\pm$ 2.9	39.0 $\pm$ 1.8	34.2 $\pm$ 0.35	53.0 $\pm$ 2.3
Tol	87.8 $\pm$ 9.6	116 $\pm$ 8.3	96.2 $\pm$ 1.2	134 $\pm$ 8.1

\* HS/GC and PT/GC/MS analyses were not statistically different at the 95% confidence level.

† Mean and standard deviation for triplicate samples.

All samples were analyzed immediately after extraction, except for the second set of subsamples taken from the Clarkson TCE-contaminated soil, which were analyzed 1 day later.

#### Data analysis

The method comparison was based on single determinations for each subsample because of analysis time limitations and because low-level samples were sacrificed when analyzed by PT/GC/MS. Results of the inter-method comparison

for the laboratory vapor-fortified soils are shown in Tables 4 and 5. These tables include the means and standard deviations of the analysis of triplicate subsamples over two exposure periods at the four vapor treatment levels. Results for the 45-day exposure of the Point Barrow, Alaska, soil are missing owing to instrument problems with the PT/GC/MS. A similar problem was experienced for the USATHAMA soil fortified with the 1:20 treatment solution; however, only a single replicate was affected. In the *Field Samples* section, Table 7 shows

**Table 5. Inter-method comparison of TDCE, Ben, TCE and Tol ( $\mu\text{g/g}$ ) for low-level fortified soils.**

**a. Mean concentrations and standard deviations for vapor treatment, 1:10 mixture of MeOH stock and tetraglyme ( $\mu\text{g/g}$ )**

	4 days exposure		46 days exposure	
	HS/GC	PT/GC/MS	HS/GC	PT/GC/MS
<b>USATHAMA standard soil</b>				
TDCE	0.195 $\pm$ 0.020	0.383 $\pm$ 0.062	0.154 $\pm$ 0.036	0.269 $\pm$ 0.103*
Ben	1.11 $\pm$ 0.040	1.21 $\pm$ 0.143*	1.02 $\pm$ 0.107	1.06 $\pm$ 0.214*
TCE	1.09 $\pm$ 0.040	1.35 $\pm$ 0.107	1.05 $\pm$ 0.124	1.15 $\pm$ 0.306*
Tol	6.43 $\pm$ 0.25	8.87 $\pm$ 0.93	7.60 $\pm$ 0.33	7.70 $\pm$ 1.85*
<b>Point Barrow, Alaska, soil</b>				
TDCE	0.939 $\pm$ 0.113	1.11 $\pm$ 0.322*	0.550 $\pm$ 0.037	0.953 $\pm$ 0.247
Ben	1.67 $\pm$ 0.125	2.05 $\pm$ 0.340*	1.60 $\pm$ 0.095	1.98 $\pm$ 0.246
TCE	2.80 $\pm$ 0.250	3.10 $\pm$ 0.485*	2.54 $\pm$ 0.35	3.36 $\pm$ 0.422
Tol	9.97 $\pm$ 0.67	11.5 $\pm$ 0.62	9.29 $\pm$ 0.32	12.4 $\pm$ 0.31

**b. Mean concentrations and standard deviations for vapor treatment, 1:20 mixture of MeOH stock and tetraglyme ( $\mu\text{g/g}$ )**

	4 days exposure		46 days exposure	
	HS/GC	PT/GC/MS	HS/GC	PT/GC/MS
<b>USATHAMA standard soil</b>				
TDCE	0.135 $\pm$ 0.017†	0.290 $\pm$ 0.080	0.084 $\pm$ 0.012	0.150 $\pm$ 0.055*
Ben	0.801 $\pm$ 0.084	0.915 $\pm$ 0.007*	0.715 $\pm$ 0.059	0.729 $\pm$ 0.188*
TCE	0.733 $\pm$ 0.073	0.873 $\pm$ 0.057*	0.599 $\pm$ 0.065	0.697 $\pm$ 0.195*
Tol	5.10 $\pm$ 0.31	4.47 $\pm$ 0.34*	5.71 $\pm$ 0.38	4.78 $\pm$ 0.81*
<b>Point Barrow Alaska soil</b>				
TDCE	0.488 $\pm$ 0.007	0.690 $\pm$ 0.016	0.385 $\pm$ 0.029	NA††
Ben	1.01 $\pm$ 0.024	1.20 $\pm$ 0.038	1.03 $\pm$ 0.085	NA
TCE	1.39 $\pm$ 0.035	1.72 $\pm$ 0.064	1.48 $\pm$ 0.11	NA
Tol	5.33 $\pm$ 0.069	6.16 $\pm$ 0.33	5.86 $\pm$ 0.37	NA

\* HS/GC and PT/GC/MS analyses were not statistically different at the 95% confidence level.

† Mean and standard deviation for triplicate samples.

†† Instrument failure.

the results obtained for the field-contaminated soils collected from the two sites where there was long-term exposure to TCE. We compared mean concentrations using student's *t*-test after determining if the variances were homogeneous with an *F*-ratio test. Where variances were not homogeneous, the larger variance was used in the *t*-test. Additionally, the Dixon outlier test was performed on the quintuplicate subsamples of the CRREL soil (Dixon 1953). All statistical tests were conducted at the 95% confidence level.

## RESULTS AND DISCUSSION

### Laboratory-fortified soils

Results of the inter-method comparison for the laboratory-fortified soils are shown in Tables 4 and 5 (and in Appendix A). Both methods produced no false negatives. Overall, analytical precision was better with the aqueous extraction-HS/GC method. The Relative Standard Deviations (RSD) for analysis of the high-level samples by aqueous-HS/GC ranged from 1.0 to 11%, with a mean of 5%, while

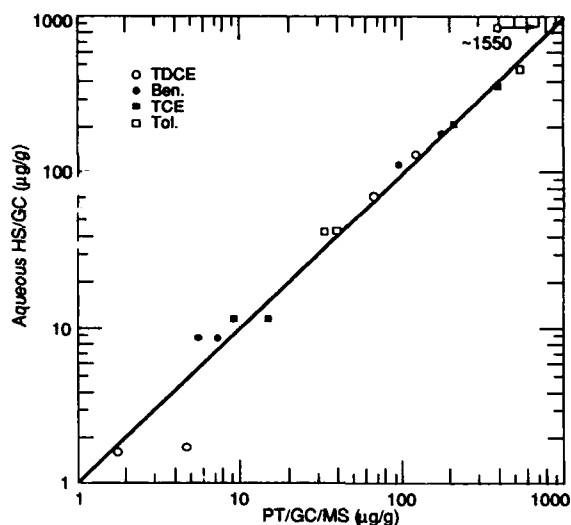


Figure 2. Log-log plot of mean concentrations ( $\mu\text{g/g}$ ) of all high-level VOC determinations in the fortified USATHAMA soil.

RSDs for MeOH-PT/GC/MS ranged from 0.5 to 36%, with a mean of 12%. Similarly, for the low-level comparison the RSDs ranged from 1.3 to 23%, with a mean of 7.9%, for aqueous-HS/GC, and from 0.76 to 38%, with a mean of 16%, for MeOH-PT/GC/MS.

The statistical comparison of means for high-level samples is included in Table 4. For the USATHAMA fortified soil, the mean values were not significantly different in 11 of the 16 comparisons. In three cases, the HS/GC method resulted in higher mean values, while PT/GC/MS resulted in higher mean values twice. Similarly, there was no pattern with length of treatment. A plot of the mean concentrations obtained by the two methods appears in Figure 2. The correlation coefficient for this linear regression is 0.964, with a slope of 0.556. However, with the omission of the single highest concentration value, which disproportionately skews the linear regression, the correlation is 0.997, with a slope of 0.948. Clearly, there is good agreement between these two methods for the determination of TDCE, TCE, Ben and Tol in the USATHAMA standard soil.

The results for Point Barrow soil at high-levels of fortification are quite different, however. Here, 11 of the 16 mean comparisons were significantly different at the 95% confidence level. In 10 of these cases, the mean MeOH-PT/GC/MS concentrations were higher on the average by 33%. A plot of the mean concentrations obtained by the two methods

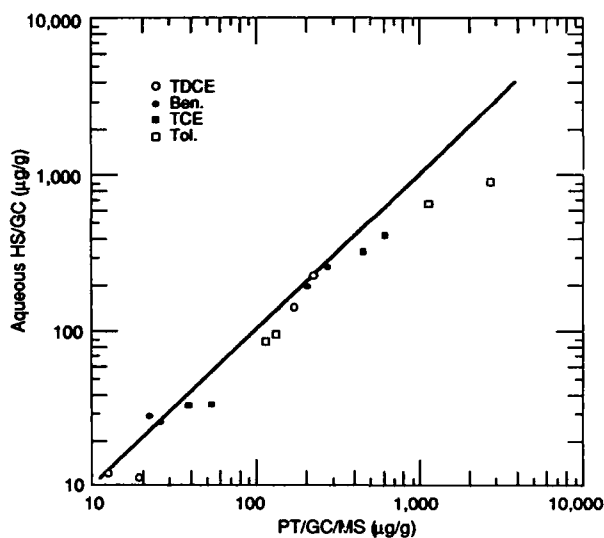


Figure 3. Log-log plot of mean concentrations ( $\mu\text{g/g}$ ) of all high-level VOC determinations in the fortified Point Barrow soil.

for this soil appears in Figure 3. Here the plot shows that the majority of points fall below the unity axis, another means of demonstrating that the MeOH-PT/GC/MS analysis generally estimated greater soil VOC concentrations. For this soil the overall average VOC concentration differences between these two methods (19%) increased with time, from 11 to 26%. When we group Ben and TDCE, and TCE and Tol, separating the compounds with the two lowest and two highest  $K_{ow}$ 's (Table 1), plots of the mean concentrations determined by the two methods show very different behavior (Fig. 4 and 5). The linear regression of the mean TDCE and Ben concentrations had a correlation coefficient of 0.993 and slope of 0.944, while the plot of the mean TCE and Tol concentrations again shows the majority of points below the unity axis. Water being less able to extract these hydrophobic VOCs is not surprising and agrees with previous works (Karickhoff et al. 1979, Chiou et al. 1983, Kiang and Grob 1986, Boyd and Sun 1990), which have addressed the influence of soil organic matter on partition coefficients. Thus, the difference in method performance with the two soils is probably caused by the high (6.69%) organic carbon in Point Barrow soil, compared to 1.45% in the USATHAMA soil.

The method comparison showed similar trends with the low-level samples; no consistent differences were found for all analytes in the USATHAMA soil or for Ben and TDCE in Point Barrow soil, but differences were observed for TCE

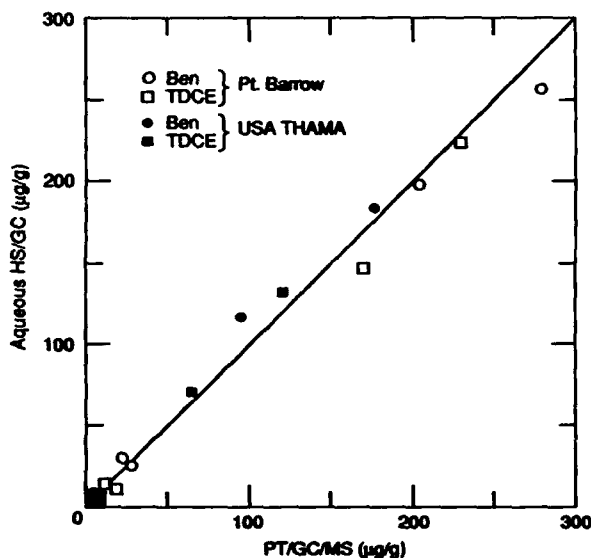


Figure 4. Linear plot of mean ( $\mu\text{g/g}$ ) TDCE and Ben concentrations in fortified soils.

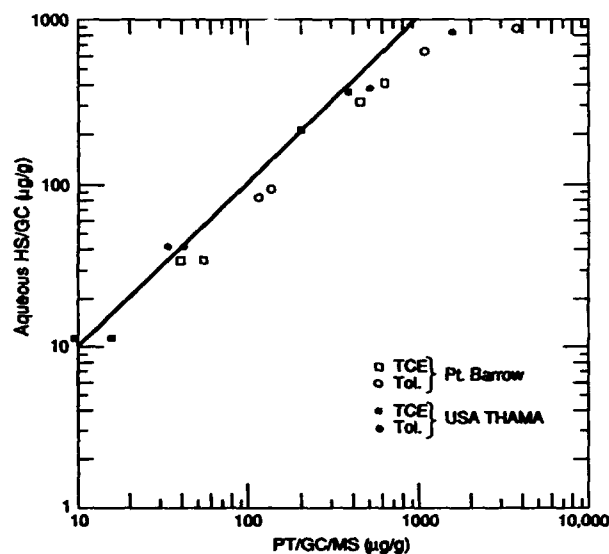


Figure 5. Log-log plot of mean ( $\mu\text{g/g}$ ) TCE and Tol concentrations in fortified soils.

Table 6. Summary of the ANOVA and LSD determinations for average HS/GC responses of spiked aqueous and soil slurry samples. Samples with common underlining are not different at the 95% confidence level as determined by the LSD.

Compound	Sample		
TDCE (LSD = 6.14)	Point Barrow*	Aqueous†	USATHAMA*
	111	113.5	116
Ben (LSD = 5.12)	Point Barrow	Aqueous	USATHAMA
	60.5	63	63
TCE (LSD = 7.82)	Point Barrow	USATHAMA	Aqueous
	69	79.5	80
Tol (LSD = 7.03)	Point Barrow	USATHAMA	Aqueous
	59.5	68	70

\* Soil present a 2 g to 30 mL aqueous slurry.

† 30 mL of water.

and Tol in that soil. Here, the difference can be attributed to the physical process of VOC extraction, since both methods use water. To demonstrate how static sample preparation can suppress HS concentrations, duplicate vials containing water (30 mL) and soil slurries representative of the fortified samples (i.e., 2 g soil/30 mL water) were spiked with a MeOH standard containing the four

VOCs. The HS/GC responses after shaking were subjected to a one-way Analysis of Variance (ANOVA) and a Least-Significant-Differences (LSD) test at the 95% confidence level. The LSD results show that both the TCE and Tol responses for the Point Barrow soil slurries were significantly lower than either the aqueous solution or USATHAMA soil slurries (Table 6). Thus, the organic matter preferentially sorbs these two compounds from solution, limiting the amount that can partition with the gaseous phase under static conditions. In contrast, a dynamic extraction is more efficient since partitioned VOCs are vapor stripped, disallowing a static equilibrium condition.

#### Field samples

The methods were compared with nine subsample sets of two field soils contaminated with TCE (Table 7). Both methods of analysis showed no false negatives; however, different analyte variances for the two soils were apparent. The large variations for the CRREL soil demonstrate the problem of inter-method comparisons using field soils that are heterogeneous. No significant differences were found between the two methods for CRREL soil because of the analyte spatial variability (Table 7). For the Clarkson soil, however, good sample precision produced statistically different means in every case, with the mean concentrations obtained by

**Table 7. Inter-method comparison for TCE concentrations ( $\mu\text{g/g}$ ) in field contaminated soil.**

	HS/GC	PT/GC/MS
<i>a. High-level comparison</i>		
<b>CRREL soil</b>		
Subsample set 1	18.3, 11.4, 6.47, 3.60, 10.7 10.1 $\pm$ 5.58*	83.5,† 3.31, 28.7, 4.33, 2.51 9.71 $\pm$ 12.7**
Subsample set 2	14.3, 9.00, 4.86, 12.3, 16.8 11.4 $\pm$ 4.66	4.40, 11.7, 36.0, 45.5, 36.9 26.9 $\pm$ 17.8**
Subsample set 3	4.42, 3.36, 2.87, 4.07, 1.60 3.26 $\pm$ 1.11	2.50, 1.23, 3.55, 80.7,† 3.69 2.74 $\pm$ 1.14**
Subsample set 4	0.68, 1.14, 1.42, 1.57, 0.72 1.11 $\pm$ 0.402	0.65, 0.70, 3.46,† 0.70, 0.36 0.60 $\pm$ 0.16**
Subsample set 5	1.42, 0.89, 13.8, 10.2, 4.39 6.14 $\pm$ 5.66	0.44, 1.18, 2.07, 1.71, 7.83* 1.35 $\pm$ 0.71**
<b>Clarkson Soil</b>		
Subsample set 1 (2 days)	3.83, 3.44, 4.17 3.81 $\pm$ 0.37	8.77, 9.89, 11.5 10.0 $\pm$ 1.37
Subsample set 2 (11 days)	3.45, 3.54, 3.81 3.60 $\pm$ 0.19	7.87, 7.71, 8.07 7.88 $\pm$ 0.18
Subsample set 3 (165 days)	2.38, 3.16, 2.66 2.73 $\pm$ 0.40	3.54, 4.36, 4.16 4.02 $\pm$ 0.43
<i>b. Low-level comparison</i>		
<b>CRREL soil</b>		
Subsamples	0.172, 0.171, 0.132, 0.288, 0.133 0.179 $\pm$ 0.064	0.188, 0.066, 0.261, 0.289, 0.274 0.216 $\pm$ 0.092**

\* Average and standard deviation.

† Outlier value as determined by Dixon's test (Dixon 1953), at the 95% confidence level.

\*\* HS/GC and PT/GC/MS analyses were not statistically different at the 95% confidence level.

aqueous-HS/GC always less than the MeOH-PT/GC/MS values. Here, the difference is not as likely attributable to the organic matter present in Clarkson soil (Table 2), as to slow desorption kinetics (Smith et al. 1990, Sawhney and Gent 1990, Pavlostathis and Jaglal 1991).

To determine whether the low results obtained by the aqueous-HS/GC method for the Clarkson soil are caused by slow kinetics or low aqueous

partition coefficients, the following test was conducted on the third subset analyzed. After the initial headspace analysis, two of the soil samples were re-extracted twice with water. The soil and water phases were separated by centrifuging the suspensions at 2300 rpm for 10 minutes. Only 28 of the 30 mL was recovered and replaced. Results were corrected for this small carryover. As previously, the samples were analyzed after 10 minutes

**Table 8. Concentrations ( $\mu\text{g/g}$ ) of TCE in HS samples after cumulative agitation or repeated aqueous extraction of the Clarkson soil, or both.**

Subsample	Extraction			Total
	1st	2nd	3rd	
W1 *	2.38	1.24	0.62	4.24
W2 †	4.14			4.14
W3 *	2.66	1.53	0.69	4.88
			$\bar{X} = 4.42 \pm 0.40$	

\* Analyzed after 10 minutes of sample agitation and after each sequential extraction.

† Analyzed after 30 minutes of cumulative sample agitation, done at 10-minute intervals over the course of 6 hours.

of agitation, since additional agitation showed no discernable increase in the headspace concentration. The third replicate never had the partition solution changed, but experienced all of the physical agitation received by the other two subsamples. A 6-hour period lapsed between the initial and final analyses for all of these subsamples. The results of this test are presented in Table 8. Clearly, equilibrium had not been nearly achieved after 10 minutes of agitation and the low results are attributable to slow desorption kinetics. In addition, comparison of the mean of these three determinations ( $4.42 \pm 0.40$ ) with the mean of the MeOH-PT/GC/MS ( $4.02 \pm 0.43$ ) shows no statistical difference. This finding agrees with these earlier studies (Smith et al. 1990, Sawhney and Gent 1990, Pavlostathis and Jaglal 1991), and emphasizes that the extraction of soil VOCs in some cases is sensitive to the degree of agitation and length of equilibration.

#### Screening for VOCs in soils

This evaluation of VOCs in fortified and field soil samples probes beyond the objective of field screening, and reveals some of the limitations and strengths of the aqueous-HS sample preparation and portable GC analysis when compared to a laboratory method (U.S. EPA 1986). With regard to this study, the water extraction-HS sample preparation and portable GC analysis technique always produced results comparable to PT/GC/MS. The largest discrepancies in concentrations for this inter-method comparison were for a soil with unusually high organic carbon content, and for a soil that had previously demonstrated slow aqueous desorption of VOCs (Pavlostathis and Jaglal 1991). Even in these two cases, aqueous extraction-HS/GC analysis provided concentration estimates that were greater than 30% of those determined by PT/GC/MS

analysis following MeOH extraction, which may certainly be deemed adequate for screening purposes.

Inhomogeneity of VOCs in soils, as demonstrated by the TCE levels in the CRREL soil, dictates that several subsamples or composite samples be taken for proper site assessment. The costs of doing PT/GC/MS analyses may limit the number of samples collected for laboratory analysis, thereby reducing the ability to assess analyte variability at discrete locations. A simple field procedure, although providing somewhat less accurate VOC concentrations, allows for more intensive sampling, i.e., more representative evaluation of contaminant distribution. Analysis by either aqueous-HS/GC or PT/GC/MS may be of equal merit if individual subsamples were taken for VOC concentrations in inhomogeneous soils.

#### SUMMARY

From its inception, researchers using headspace sample preparation and analysis with a portable gas chromatograph (HS/GC) recognized storage and transfer problems. In this study, emphasis has been put on the aqueous HS sample preparation procedure, rather than the method of portable GC detection because aqueous-HS/portable GC analysis often will have to be tailored to the VOCs present at a given site. Typically, this task can be done based on the site's history, but there will be instances of minimal history where a more qualitative method of analysis will have to proceed. Once the VOCs of concern have been identified, aqueous-HS/GC analysis fills a void between litigation quality analysis of discrete soil samples and the preliminary monitoring that is necessary for personnel safety or for the delineation of areas with high VOC vapor concentrations. Although human safety surveys and contour mapping of ambient or soil gas concentrations are prudent and often necessary, they are unreliable indicators of VOC concentrations present in soil samples (Smith et al. 1990).

Preparing laboratory samples by vapor fortification allows for a more rigorous method of evaluation than is possible with procedures currently practiced in quality assurance programs. Since no VOC soil standards exist at present for the SV-846 program (Zarrabi et al. 1991), the assessment of sample determination accuracy relies on solution spike and recovery tests. The volatility of VOCs has made matrix spiking a difficult task. Generally, VOC spiking is done by introducing doped MeOH

aliquots directly to the purge chamber of a purge-and-trap system that contains the matrix sample of concern. This method is of dubious validity for it only evaluates the determinative step, and it provides no opportunity for natural sorptive processes to take place. Soils fortified by vapor treatment require both an extraction and determinative step, thus providing a more comprehensive evaluation of a method's capability. Our statistical analysis showed no consistent significant difference between aqueous-HS/GC and PT/GC/MS for a soil fortified with low organic carbon. Also, there were no consistent difference for the two compounds with the lowest octanol/water partition coefficients in either fortified soil tested, or for TCE in the CRREL soil. Thus, for many cases the methods are not expected to be significantly different in terms of accuracy, but there may be differences in other cases.

Compared to the current SW-846 program method 8240 guidelines for the analysis of VOCs in soils (U.S. EPA 1986), the aqueous-HS/GC method described here avoids some of the potential losses during sample preparation, since it has been shown that greater than 80% of the VOCs in a soil sample can be lost when contract laboratories acquire subsamples from bulk soils shipped from the field (Urban et al. 1989, Siegrist and Jennsen 1990). Universal acceptance of procedures requiring the rapid placement of soils into vessels containing extraction solvents or that do not allow vapors loss, and the recognition of field analysis methods, will improve the reliability of soil VOC determinations.

## CONCLUSION

Compared to EPA Method 8240, aqueous extraction-HS sample preparation and portable GC analysis for VOCs in soils is quicker, more field compatible and economical, does not require the use of hazardous chemicals, and covers the same range of concentrations with a single sample preparation procedure. HS/GC also minimizes sample handling and lag time between collection and analysis, thereby reducing the possibility of false negatives, a problem with soil samples that were stored and rehandled prior to analysis. As with any field method, limitations need to be clearly established so that the results are appropriately interpreted. However, with regard to soil sample screening, aqueous-HS sample preparation and portable GC analysis is a valuable tool, allowing for a better use of analytical resources and funds for the assess-

ment and remediation of hazardous waste sites. Use of this field-transportable analysis method would potentially increase the reliability of soil VOC determinations by allowing for more sample-intensive site investigations and avoiding the common practice of transporting, storing and disturbing collected soils.

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**APPENDIX A: ANALYTE CONCENTRATIONS DETERMINED FOR INDIVIDUAL  
SUBSAMPLES OF THE LABORATORY FORTIFIED SAMPLE SETS**

**Set 1—100% MeOH Stock**

Compound	USATHAMA soil											
	HS/GC ( $\mu\text{g/g}$ )						PT/GC/MS ( $\mu\text{g/g}$ )					
	4 days			39 days			4 days			39 days		
TDCE	66.0	76.2	76.2	147	126	131	67	68	63	114	108	143
Ben	111	117	124	179	186	186	92.7	96.8	93.5	156	158	216
TCE	208	208	225	363	372	382	208	214	184	311	328	501
Tol	480	480	516	835	885	935	564	559	465	1400	1420	2150

Compound	Point Barrow soil											
	HS/GC ( $\mu\text{g/g}$ )						PT/GC/MS ( $\mu\text{g/g}$ )					
	4 days			39 days			4 days			39 days		
TDCE	152	148	144	228	233	213	162	168	181	228	243	219
Ben	192	210	192	256	270	242	199	209	204	244	299	300
TCE	303	350	303	419	438	391	431	445	456	549	632	658
Tol	606	756	703	935	985	860	1110	1120	1120	2790	2670	2750

**Set 2—50% MeOH Stock /50% Tetraglyme**

Compound	USATHAMA soil											
	HS/GC ( $\mu\text{g/g}$ )						PT/GC/MS ( $\mu\text{g/g}$ )					
	4 days			39 days			4 days			39 days		
TDCE	1.74	1.62	1.52	1.88	1.66	1.59	1.24	1.72	2.55	4.88	3.6	6.29
Ben	8.97	8.64	8.64	8.80	8.64	8.80	4.17	6.30	6.53	8.80	8.64	8.80
TCE	11.7	12.1	11.3	11.8	11.3	11.8	7.30	9.95	10.4	15.4	12.6	17.4
Tol	42.0	44.6	42.0	42.4	41.8	45.9	28.9	35.2	35.7	40.6	37.0	46.7

Compound	Point Barrow soil											
	HS/GC ( $\mu\text{g/g}$ )						PT/GC/MS ( $\mu\text{g/g}$ )					
	4 days			39 days			4 days			39 days		
TDCE	11.8	12.5	12.5	12.2	12.0	10.9	11.2	14.5	11.8	19.8	19.2	18.4
Ben	27.0	28.0	32.4	26.5	27.0	26.5	19.4	25.3	21.4	27.3	27.0	23.8
TCE	32.0	33.0	37.4	34.0	34.6	34.0	38.2	41.0	37.7	55.4	50.9	52.8
Tol	81.2	83.4	98.8	96.9	94.9	96.9	114	126	110	143	127	133

**Set 3—10% MeOH Stock /90% tetraglyme**

Compound	USATHAMA soil											
	HS/GC (ng/g)						PT/GC/MS (ng/g)					
	4 days			46 days			4 days			46 days		
TDCE	179	218	188	193	146	123	404	432	313	335	321	150
Ben	1090	1160	1090	1140	1000	930	1340	1250	1060	1220	1140	816
TCE	1090	1130	1050	1180	1020	936	1440	1370	1230	1290	1360	799
Tol	6510	6630	6150	7980	7410	7410	9920	8150	8540	8540	8970	5580

Compound	Point Barrow soil						PT/GC/MS (µg/g)					
	HS/GC (µg/g)						PT/GC/MS (µg/g)					
	4 days			46 days			4 days			46 days		
TDCE	1.06	0.921	0.837	0.558	0.558	0.510	1.48	0.900	0.947	1.69	1.61	1.50
Ben	1.77	1.71	1.53	1.69	1.61	1.50	2.44	1.92	1.80	1.90	2.26	1.79
TCE	2.97	2.91	2.51	2.66	2.53	2.42	3.66	2.88	2.77	3.27	3.82	2.99
Tol	10.2	10.5	9.21	9.66	9.12	9.09	11.7	12.0	10.8	12.5	12.7	12.1

**Set 4—5% MeOH Stock /95% tetraglyme**

Compound	USATHAMA soil						PT/GC/MS (ng/g)					
	HS/GC (ng/g)						PT/GC/MS (ng/g)					
	4 days			46 days			4 days			46 days		
TDCE	123	128	154	70.8	89.4	93.0	346	233		87.0	190	172
Ben	744	762	897	648	756	741	920	910		517	875	795
TCE	669	717	813	525	645	627	913	833		484	865	743
Tol	4920	4920	5460	5310	6060	5760	4230	4710		3860	5400	5080

Compound	Point Barrow soil						PT/GC/MS (ng/g)					
	HS/GC (ng/g)						PT/GC/MS (ng/g)					
	4 days			46 days			4 days			46 days		
TDCE	492	492	480	384	357	414	693	673	704		NA	
Ben	978	1020	1020	1020	951	1120	1210	1160	1240		NA	
TCE	1370	1370	1430	1470	1380	1600	1730	1660	1780		NA	
Tol	5250	5370	5370	5760	5550	6270	6170	5820	6480		NA	

# REPORT DOCUMENTATION PAGE

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